

CORRELATION OF COAL LIQUEFACTION REACTIVITY WITH COAL PROPERTIES

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ABSTRACT

A narrow suite of bituminous coals chosen from the DOE/Penn State sample bank has been hydrogenated in a batch stirred autoclave. Rates of conversion to THF-solubles have been measured, and the data modeled using a pseudo-second order rate expression. Extent of conversion and rate of conversion of the coals in the suite have been correlated to coal compositional parameters and structural features. Recent data on reactivity correlations with information from pyrolysis/mass spectrometry and C-NMR are presented.

INTRODUCTION

The relationship between coal composition and hydrogenation reactivity has been studied extensively for over 60 years. As early as 1920, Bergius (1) recognized that coal with less than 85% carbon (daf) made poor liquefaction feedstocks. Francis (2) suggested that reactivity was related to rank, and many other researchers have attempted to correlate reactivity with rank (3,4,5). Neavel (6) has shown that a relationship does exist between rank and rate of coal hydrogenation to benzene solubles. Fischer (7) and his co-workers at the Bureau of Mines in Bruceton developed mathematical models for coal liquefaction reactivity based on a petrographic analysis of the parent coal. This concept was expanded and greatly elaborated upon by Given et al. (8,9,10,11), who established reactivity ensamples by statistical factor analysis of a large number of samples. Recently, Furlong et al. (12) studied the use of different definitions for coal reactivity, and demonstrated the utility of a definition based on kinetic parameters when ranking coals of very similar properties.

All studies relating coal properties to coal hydrogenation reactivity are hampered by the crude tools available for chemical and structural analysis of the prime reactant. Pyrolysis, followed by mass spectroscopy (Py/MS) of the products at low energy levels provides a new tool for coal analysis that can provide data on structural features that previously could not be obtained (13). Voorhees et al. (14), and Meuzelaar et al. (15) have recently reported correlations of structural data from coal Py/MS and coal hydrol liquefaction reactivity.

EXPERIMENTAL

A series of bituminous coals from the DOE/Penn State sample bank were hydrogenated in a batch stirred autoclave reactor into which coal was injected. Table 1 presents data on coal properties in the suite. All coals were low sulfur, in order to minimize catalytic effects due to H₂S and iron pyrite. Details of the run procedure and reaction equipment used have been presented elsewhere (12). Coal samples were pyrolysed using a Fisher Curie-Point pyrolyser in conjunction with an Extra-nuclear SpectrEL mass spectrometer. Curie point wires composed of Ni (510 C final temperature) and low energy (14 ev) electron impact were used throughout for data acquisition. Mass spectral data were collected on a Hewlett-Packard 2100 S computer, and the data then analysed using ARTHUR (Infomatrix Inc., Seattle, Wa.). Solid state ¹³C-NMR was performed at the NSF Regional Center for NMR at Colorado State University, Department of Chemistry.

DISCUSSION AND RESULTS

Rate data on coal conversion to THF-solubles was reduced using a pseudo-second

order kinetic model of the form:

$$\frac{dC}{dt} = -k_f C^2 + k_r P^2$$

Here k_f and k_r (with units: mass fraction $\cdot \text{min}^{-1}$) are the forward and reverse rate constants for the reaction:



As previously, coal (C) was defined in these expressions as THF-insoluble organic matter, which included unreacted coal as well as high-molecular-weight moieties and coke produced by free radical recombination and condensation reactions. Parameter P was defined as all products soluble in THF.

Using conversion (X) defined as the fraction of coal reacted to THF-soluble materials, the mass balance may be rewritten as a function of the conversion:

$$\frac{1}{k_f} \frac{dX}{dt} = (-X)^2 - \left[\frac{1}{K} \right] X^2$$

Here $C = 1 - X$, $P = X$, and K , the equilibrium constant for the reaction, is given by k_f/k_r .

Data for each of the 11 coals which were successfully run were processed by non-linear parameter estimation methods (16) to obtain values for the parameters k_f and k_r in the second-order model. These data are given in Table 2 as are values for the equilibrium constant K . Also in Table 2 are values for the 60 min conversion to THF-soluble materials (X(60)).

Data on the aliphatic-to-aromatic carbon ratios in the parent coal samples plotted against kinetic reactivity (k_f) are shown in Figure 1. With one exception, the correlation is one of increasing reactivity with increasing aliphatic to aromatic carbon ratio. This was to be expected, as it has been well established that the more aliphatic coals convert more readily in comparison with the more aromatic coals. The correlation with rate of conversion (Figure 1) is fairly good, thus substantiating the importance of aliphatic carbon-carbon bonds in coal hydrogenation. Aliphatic/aromatic carbon ratio also correlates fairly well with extent of reaction (X(60)), but not with reactivity as measured by the pseudo-equilibrium constant (K) from Table 2. Overall however, the correlation of aliphatic to aromatic carbon is the best with reactivity as defined in a kinetic fashion by the forward rate constant.

Coals from the reactivity suite shown in Table 1 were run in triplicate on the Py/MS, and an average spectrum obtained which represented a composite spectrum for 9 of the 11 coal hydrogenated. Data from Py/MS of the coal suite were reduced by ARTHUR, and a statistical factor analysis performed on the entire data set. From the factor analysis, 4 factors were identified which accounted for over 72% of the variation in the data set. The factors and the percent of total variation explained were as follows:

FACTOR	VARIATION ACCOUNTED FOR	CUMULATIVE VARIATION
1	24.3%	24.3%
2	23.1%	47.4%
3	14.8%	62.1%
4	10.0%	72.2%

These factors were utilized in Karhunen Loeve (K-L) plots obtained from ARTHUR, in order to ascertain whether any clustering into reactivity groupings could be obtained. As shown in Figure 2, a plot of K-L factor 3 vs K-L factor 2 does produce such a clustering, with the higher reactivity coals in the suite falling towards the upper right hand corner of the plot, and the less reactive coals clustering in the lower left. These data may indicate the utility of pyrolysis/mass spectrometry as a rapid screening tool for coal reactivity.

The data set from Py/MS of the coal suite can be rotated towards any other factor, and composite spectra calculated which demonstrate relationships between chemical moieties in the spectrum and the chosen factor. Such correlations have

recently been reported by Baldwin (17) on a suite of coals with a very broad geographical and rank distribution. Further analysis of this data set was performed by rotating the composite spectra towards reactivity, with reactivity defined in each of the three manners listed above (k_f , $X(60)$, and K). The results of these analyses are presented in Figures 3-5. As before, the only meaningful correlation seems to be when reactivity is defined as a kinetic reactivity. Figure 3 indicates that a strong positive correlation exists between a homologous series of high molecular weight naphthalenes and coal reaction rate. Further analysis of Py/MS data set is continuing, and will be presented later.

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Table 1 Parent coal analyses

Ultimate analysis (wt % dmf (Parr))													
Coal			C	H	N	O	Min. matter	vit	Maceral comp. (vol % dmf) iner.	lipt.	Sulphur (wt % daf) pyr.	Sulphur (wt % daf) tot.	
PSOC No.	Rank	Seam											State
001	hvAb	Upper Elkhorn	KY	84.36	5.46	1.54	8.64	4.71	54.8	21.7	23.5	0.10	0.81
056	hvCb	Arizona No. 2	AZ	77.37	5.90	1.34	15.39	6.92	83.9	12.8	3.3	0.01	0.45
071	hvCb	Rogers	WA	78.00	5.88	1.68	14.44	7.41	86.5	7.7	5.8	0.07	0.58
107	hvBb	Brazil Block	IN	81.97	5.07	1.37	11.59	6.42	62.4	14.6	23.0	0.11	0.53
151	hvCb	Lower Blue	NM	78.37	5.87	1.24	14.51	5.80	78.6	10.8	10.6	0.05	0.47
437	hvAb	Utah B	UT	80.26	6.20	1.47	12.07	5.63	92.1	6.0	1.9	0.11	0.51
444	hvBb	Colorado E	CO	78.87	6.47	1.57	13.09	2.46	94.4	3.9	1.7	0.06	0.46
456	hvAb	Blind Canyon	UT	79.49	6.43	1.58	12.50	4.91	88.7	10.2	1.1	0.06	0.37
577	hvCb	(unnamed)	TX	79.97	5.68	1.32	13.04	25.51	87.2	11.7	1.1	0.17	1.17

Table 2 Estimated second-order rate parameters

Coal (PSOC No.)	k_f^*	k_r^*	K	a	x (60)
001	0.0672 ± 0.0103	0.0094 ± 0.0069	7.17	0.728	0.724
056	0.1655 ± 0.0319	0.0107 ± 0.0080	15.51	0.797	0.828
071	0.1358 ± 0.0253	0.0068 ± 0.0066	20.01	0.817	0.837
107	0.0839 ± 0.0064	0.0018 ± 0.0023	45.94	0.871	0.810
151	0.1673 ± 0.0265	0.0143 ± 0.0076	11.71	0.774	0.801
437	0.1997 ± 0.0253	0.0082 ± 0.0046	24.34	0.831	0.850
444	0.1057 ± 0.0162	0.0002 ± 0.0039	485.33	0.957	0.872
456	0.2174 ± 0.0363	0.0055 ± 0.0051	39.81	0.863	0.884
577	0.1369 ± 0.0169	0.0157 ± 0.0063	8.74	0.747	0.769

* 95% confidence limits on k_f and k_r estimates.Rate constants have units of (mass fraction min⁻¹)

FIGURE 1

ALPHA/AROMATIC CARBON RATIO VS FORWARD RATE CONSTANTS

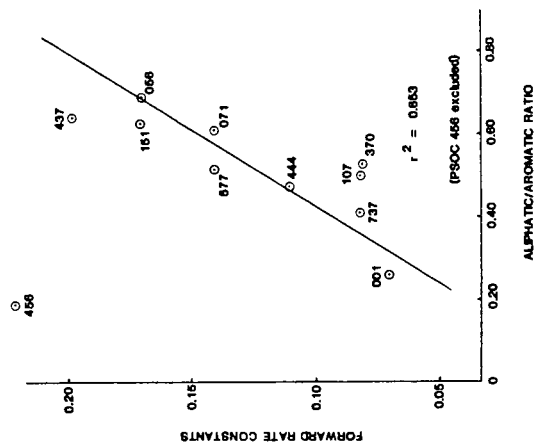


FIGURE 2

KARHUNEN-LOEVE PLOT

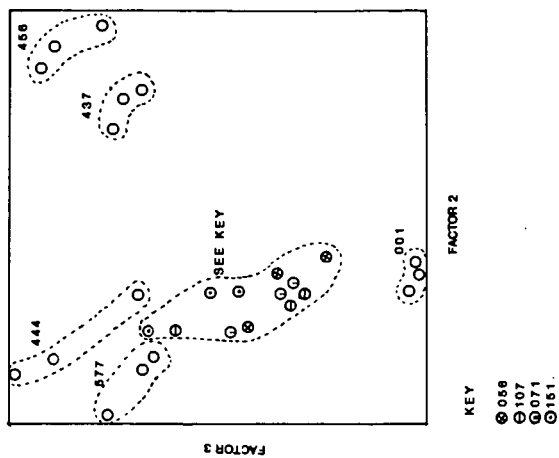


FIGURE 3

FACTOR SPECTRUM, KINETIC REACTIVITY

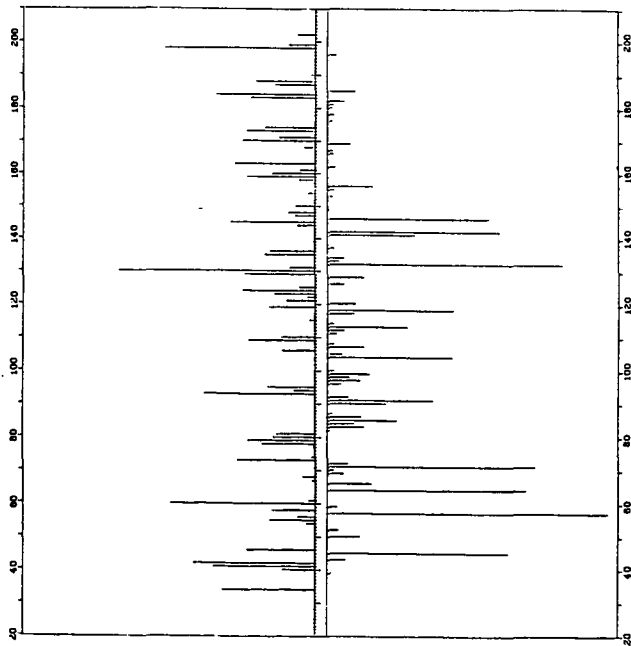


FIGURE 4

FACTOR SPECTRUM, X(60) REACTIVITY

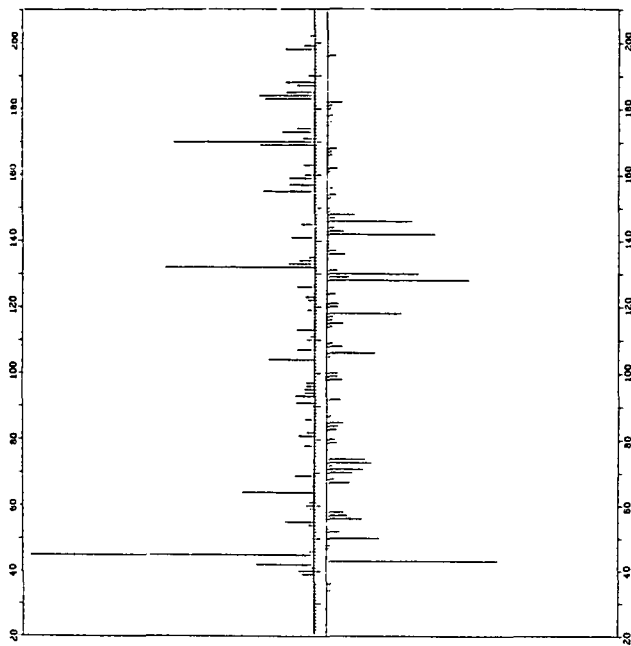
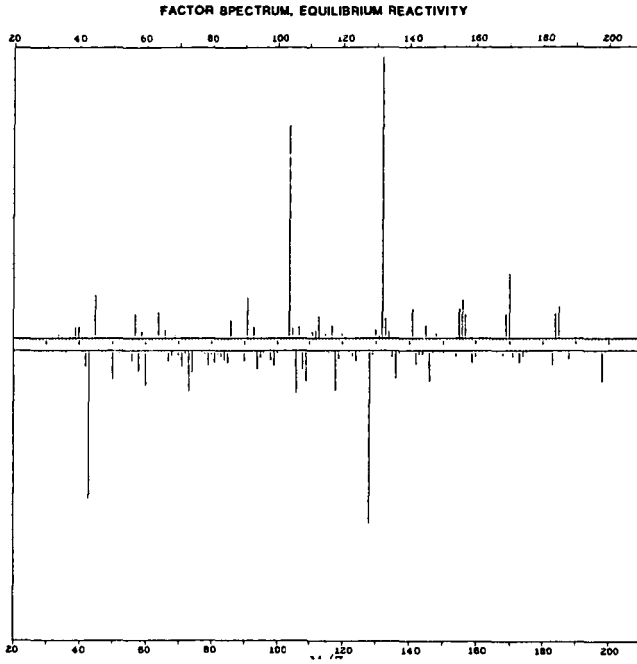


FIGURE 6



CHARACTERIZATION OF SHORT CONTACT TIME DISSOLUTION PRODUCTS
FROM A SERIES OF VITRINITE-RICH COALS

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The objective of this study is to identify the transformations that occur in coal organic structural units during liquefaction. To ensure that mainly primary reactions are being observed, the study has focused on short contact time dissolution in donor solvent media. It has been shown by Neavel that under SCT conditions a significant amount of bituminous coals can be dissolved (1). Whitehurst et al. have reported an in depth study of the SCT reaction on several coals. In our study we have examined the relationship between the compositional parameters of the coals and both their reactivity and product chemical characteristics. Given and his co-workers examined the effects of coal characteristics on longer contact time liquefaction (3-5). This work by Given is one of the first applications of statistical analysis to this type of problem. However, either benzene (3) or ethyl acetate (4,5) was used to extract the products and conversion was calculated from the weight of the insoluble residue. Since the benzene insoluble, pyridine soluble fraction, often called asphaltoids or preasphaltenes, is a key intermediate in the initial stage of coal liquefaction (6,7), we would like to correlate the solubility in hexane, benzene/ethanol, and pyridine with compositional parameters.

We have recently studied the SCT reaction of separated coal macerals (8). In order to separate the macerals by density gradient centrifugation it was necessary to demineralize the coals with HCl and HF and grind them to less than 3 microns. It has been shown that mineral matter exerts a beneficial and possibly unpredictable effect on the coal dissolution (2,9-11). To examine the effects of the demineralization and grinding, a series of 21 of the treated unseparated coals were studied. The original raw coals were obtained from the Penn State Coal Sample Bank. It was observed using multivariate analysis that product solubility, which was used to determine conversion, can be predicted from linear combinations of carbon, hydrogen, density and exinite content.

After considering these results, we felt that in order to make the study more complete, it would be useful to study another set of coals which had not been demineralized. Dr. Richard Neavel consented to supply us with a set of 25 coals from the Exxon Coal Library. These samples are essentially "premium" coals which have been protected from oxidation and are homogeneous. The preparation and some of the properties have been described (12). An advantage of using this set of coals is that other structure studies are in progress in other laboratories and in the Fundamental Chemistry of Coals program at ANL. This information will be useful in interpreting the results from the SCT reaction.

Experimental

SAMPLES Analytical data for the demineralized coals are given in Table 1. The Exxon coals are described in reference 12.

SCT REACTION Typically, 100 mg of coal sample and 300 mg of tetralin were transferred to a thick wall glass tube flushed with nitrogen, sealed, and plunged into a preheated fluidized sand bath at 419°C for 6 minutes. For the demineralized coals 60 mg coal and 240 mg of tetralin were used. After the glass tube was cooled in air and opened, the contents were washed out with hexane, agitated in an

ultrasonic bath, and centrifuged. The supernatant was removed and the insoluble part was washed with three portions of hexane. The hexane insoluble fraction was then extracted successively with portions of benzene/ethanol (1:1) mixture, and pyridine. Each insoluble fraction was dried under vacuum at 60°C (80°C for the pyridine insoluble fraction) and weighed. Conversion was calculated as follows:

$$\text{conversion (\%,daf)} = \frac{\text{wt. of coal} - \text{wt. of insoluble fraction}}{\text{wt. of coal (1-\% ash)}} \times 10^4$$

The benzene solubility was dropped for the Exxon coals when it was found that with the demineralized coals only a few percent more were soluble in benzene compared to hexane.

Approximate molecular weight or size distribution was determined by gel permeation chromatography for the benzene-ethanol soluble products for both the series of demineralized coals and for the Exxon coals. The samples were eluted with THF through a set of three ultra-styragel columns (Waters Associates) having 1,000, 500 and 100 Å nominal pore diameters respectively. The size exclusion limit was approximately 10,000. This set of columns was calibrated using several polymers and large nonpolymeric molecules that could be found in coals. The samples were detected using a UV spectrometer set at 254 nm, and the output digitized and stored using a microcomputer (DEC LSI 11/23). The data was further processed on a DEC VAX 11/780 computer.

Proton NMR data were obtained on the benzene/ethanol soluble product from the reactive Exxon coals. Pyridine-d₅ was used as the solvent and spectra were obtained on a Nicolet 200 MHz instrument. Using the measured areas under the aliphatic and aromatic regions, the fraction of aromatic carbons (fa) was determined from the Brown-Ladner equation (11).

RESULTS AND DISCUSSION

For both sets of coals the first aspect of the data which we examined was the relationship between composition of the whole coal and the yield of the soluble products. The benzene-ethanol solubility data which was calculated on a wt% of coal (dmmf) is shown in Figure 1 as a function of carbon content. A multivariate analysis was performed on this data using the Statistical Analysis System (SAS) package. The correlations observed for these samples were much poorer than those obtained for the set of demineralized coals. Some representative R² values are given for a selected combination of variables.

	Hexane		Benzene/EtOH		Pyridine	
	DC	Exxon	DC	Exxon	DC	Exxon
C	0.919	0.781	0.843	0.130	0.565	0.027
C,H	0.957	0.841	0.918	0.490	0.781	0.477

DC = demineralized coals.

A plot of predicted and observed benzene-ethanol solubility is shown in Figure 2. This difference found between the two sets of coals may be due to at least two reasons. First, the Exxon coals were not demineralized, and the effects of mineral matter on SCT dissolution may be critical and unpredictable. It should be emphasized that the Exxon coals were processed to give low mineral matter content and in the multivariate analysis, inclusion of the high mineral matter coals did not significantly affect the analysis. Secondly, there is a difference in particle

size, which should influence the variations in yields to a lesser degree. One would expect the smaller particle size samples to give a higher solubility, but it is difficult to deduce why the difference in correlation with composition results. It has been reported by Whitehurst et al. (2) that demineralization increases yields at short contact times especially for lower rank coals.

It is apparent from Figure 1 that for the lower rank coals the demineralized ones are more reactive than the untreated coals. This could account for the more predictable behavior with rank of the demineralized coals. For the Exxon coals in this study and as has been shown in other studies (2) the lower rank coals are less reactive under SCT conditions compared to the high volatile bituminous coals.

Variations observed in molecular size distribution as a function of composition appears to be more similar between the two sets of coals. A relative molecular weight or size distribution was obtained for all the coal products under identical conditions. The absolute values determined for the molecular weights cannot be trusted for coal derived materials. However, comparisons of the results from coal products run under standard conditions can be useful. An example of one of the chromatograms is shown in Figure 3. Most of the chromatograms had inflection points at molecular weights of approximately 300 and 700. All of the chromatograms were divided into three areas at 0-300, 300-700, and 700-10,000, and the relative areas of the three regions determined.

In the initial SCT study of the maceral concentrates, it was observed that the average molecular weight decreased with decreasing conversion (8). In both sets of whole coals this trend is followed. In order to look at the results in a more quantitative way, principal component analysis has been applied to these data. This approach has been eloquently described by Yarzab et al. (4). The objective of this analysis is to identify variables, such as original coal composition and molecular weight distributions, which change in a parallel fashion. The variables that meet this criteria are assigned to a "factor". A coefficient is calculated for each variable in each factor. The closer the coefficient or loading is to ± 1.0 the better the variable correlates with that factor. Loadings with opposite signs indicated that these properties are inversely correlated.

The results of the principal component analysis are shown in Tables 2 and 3 for the demineralized and Exxon coals respectively. Coefficients of less than ± 0.5 have been left out since they are less significant and it makes it easier to see the correlations. In both sets of data the carbon content is directly correlated with the LMW band and inversely with the HMW. The reverse is true for the oxygen content and for the Exxon set, volatile matter, which inversely correlates with LMW and directly with HMW. The MMW band is independent of any of the variables used in this analysis and was assigned the 4th and least significant factor. The values at the bottom of each table indicate the contribution made by each factor in explaining variance observed. It appears that the molecular distribution of the products in SCT dissolution is a function of rank. A plot of the high molecular weight area as a function of carbon content in Figure 4 appears to confirm this observation.

The fa values were determined by NMR for the benzene-ethanol solubles from the Exxon coals. Factor analysis indicated that the fa values inversely correlated with hydrogen content of the coals and with solubilities in both benzene-ethanol and pyridine. A plot of fa's as a function of hydrogen content is shown in Figure 5. These results indicate a problem with using solubility to determine conversion. As expected the more aliphatic products tend to be more soluble. The same amount of bond cleavage in a more aromatic coal could have a lower yield by solubility. From this analysis it could be expected that fa values of the products should approximately follow the solubility. This is what is observed in Figure 6. Although there is significant scatter in the points the trend is apparent.

Conclusions

Apparently yields from SCT dissolution of finely ground, demineralized coals can be more accurately predicted than with the dissolution of raw coals. Gross product chemical characteristics do not seem to differ to a large extent. Presently we are examining more detailed chemical characteristics of the various products using pyrolysis mass spectrometry with precise mass measurements.

Acknowledgements

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TABLE 1

Analytical Data for Demineralized Coals

Coal	%C ^a	%H ^a	%N ^a	%S ^a	%O ^{a,b}	%Ash	%E ^c	%V ^c	%I ^c	Density
PSOC-106	80.0	4.4	1.3	0.8	13.5	0.4	19.0	35.1	45.9	1.328
PSOC-107	78.7	4.7	1.5	0.4	14.7	0.1	13.1	69.5	17.3	1.301
PSOC-124	82.8	6.9	1.2	1.0	8.1	1.2	56.5	14.6	28.8	1.195
PSOC-151	75.0	4.9	0.8	0.4	18.9	0.3	5.5	83.9	10.5	1.322
PSOC-236	86.9	4.6	1.9	0.5	6.1	0.2	0.2	95.6	4.2	1.280
PSOC-240	67.5	5.0	1.2	1.7	24.6	0.4	4.4	92.1	3.5	1.376
PSOC-268	83.5	4.9	1.4	1.1	9.1	0.4	7.2	82.4	10.4	1.275
PSOC-285	77.5	4.9	1.4	4.4	11.8	3.3	3.0	91.5	5.6	1.276
PSOC-297	79.7	5.6	1.7	1.6	11.4	1.4	19.0	62.8	18.2	1.285
PSOC-380	89.5	3.4	1.1	0.6	5.4	0.2	0	88.6	11.4	1.357
PSOC-403	85.7	4.8	1.8	0.5	7.2	0.2	2.4	91.6	6.0	1.287
PSOC-409	87.1	4.2	1.9	1.5	5.3	1.1	6.5	86.9	6.6	1.317
PSOC-592	77.4	4.9	1.3	2.0	14.4	0.4	12.5	53.0	34.4	1.316
PSOC-594	75.0	4.8	1.2	2.7	16.3	0.5	5.1	88.5	6.6	1.322
PSOC-629	91.0	3.2	0.8	0.7	4.3	0.8	0	90.6	9.4	1.401
PSOC-852	75.3	5.0	1.7	0.4	17.6	0.0	1.9	94.0	4.2	1.309
PSOC-975	69.0	4.6	1.0	0.5	24.9	0.2	4.6	91.6	4.0	1.393
PSOC-1005	69.6	4.5	0.9	0.4	24.6	0.0	1.6	95.5	2.9	1.405
PSOC-1109	70.9	6.6	1.6	1.5	19.4	1.3	70.7	21.4	7.8	1.228
U1	77.3	5.7	1.5	0.7	14.8	1.0	10.2	85.2	4.6	1.244
SIU-744A	81.4	4.7	1.3	0.8	11.8	0.1	4.6	93.8	1.6	1.300
SIU-744B	82.2	5.1	1.4	0.8	10.5	0.3	15.4	71.0	13.6	1.271

^adry and ash free basis.^bby difference.^cE=exinite, V=vitrinite, I=inertinite.

TABLE 2. DEMINERALIZED COALS, VARIMAX ROTATED FACTOR PATTERN
FOR PRODUCT MOLECULAR WEIGHT DISTRIBUTION

	<u>Factor 1</u>	<u>Factor 2</u>	<u>Factor 3</u>	<u>Factor 4</u>
Carbon	-0.80550			
Hydrogen		0.89706		
Sulfur		0.73940		
Oxygen	0.85843			
Nitrogen	-0.81678			
HMW	0.90740			
MMW			0.94011	
LMW	-0.96976			
Density		-0.91986		
Exinite		0.85784		
Vitrinite		-0.72136		
Inertinite		0.86206		
Pyridine Sol.	0.89258			

Variance explained by each factor:

Factor 1, 4.836022; Factor 2, 3.347514; Factor 3, 1.793194; Factor 4, 1.681776

TABLE 3. EXXON COAL VARIMAX ROTATED FACTOR PATTERN FOR PRODUCT
MOLECULAR WEIGHT DISTRIBUTION

	<u>Factor 1</u>	<u>Factor 2</u>	<u>Factor 3</u>	<u>Factor 4</u>
Carbon	-0.85545			
Hydrogen		0.91672		
Sulfur		0.65336	0.53082	
Oxygen	0.79685			
VM	0.89172			
MM		0.93145		
Inert		0.70451		
HMW	0.91429			
MMW			0.96824	
LMW	-0.88076			

Variance Explained by Each Factor:
Factor 3, 1.756227; Factor 4, 1.258782

Factor 1, 3.980301; Factor 2, 2.006584;

Figure 1. Product solubility in benzene-ethanol as a function of carbon content.

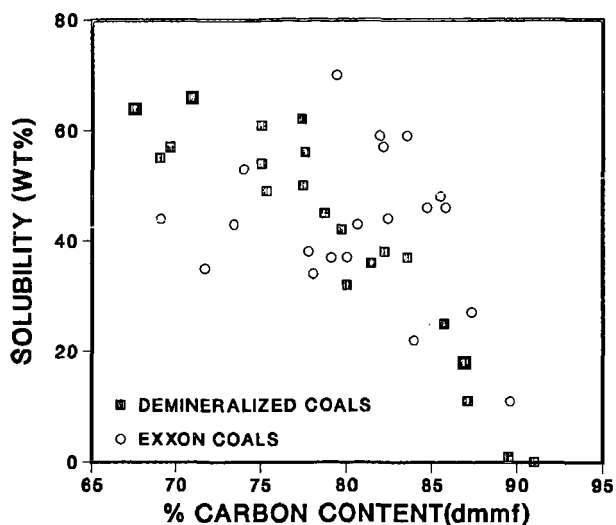


Figure 2. Predicted benzene-ethanol solubilities from multivariate least squares analysis using C and H content.

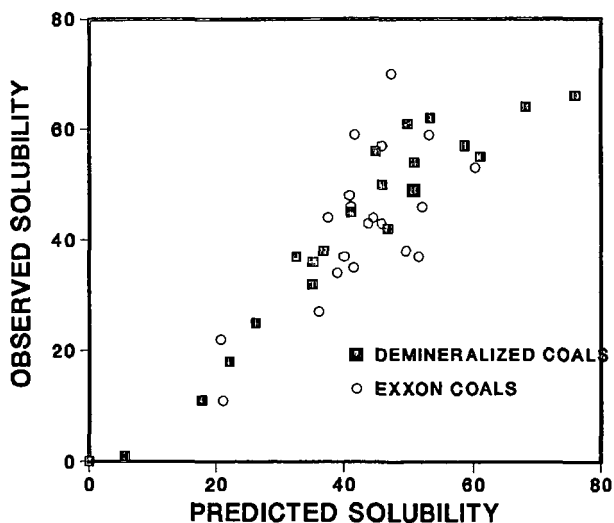


Figure 3. GPC of the benzene-ethanol soluble portion from a demineralized coal(psoc 107).

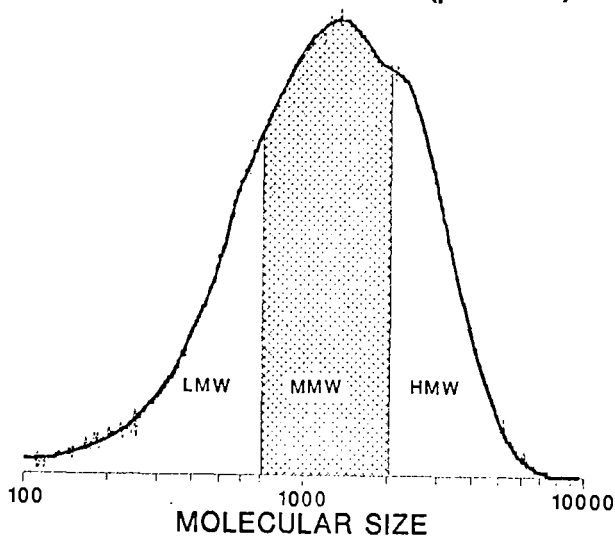


Figure 4. The change in relative amounts of high molecular species with carbon content of the coals.

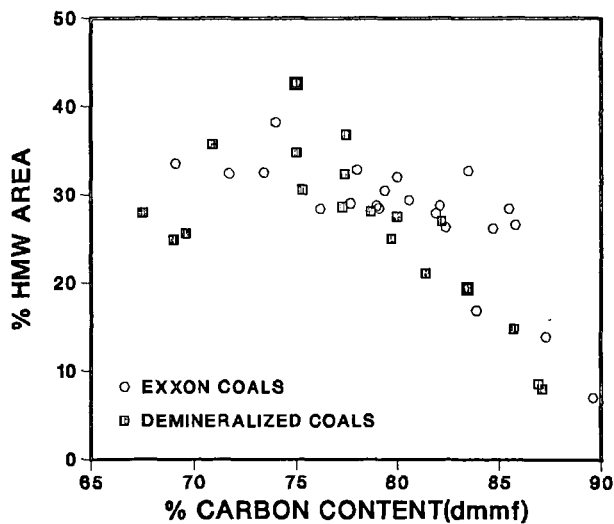


Figure 5. Variation of the fa of benzene-ethanol solubles with hydrogen content for Exxon coals.

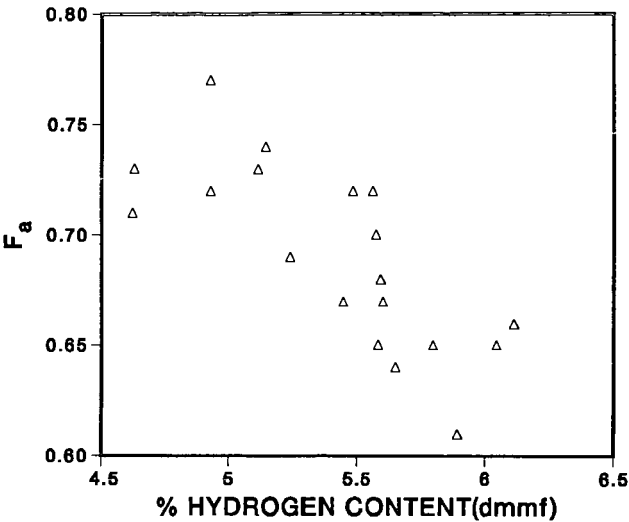
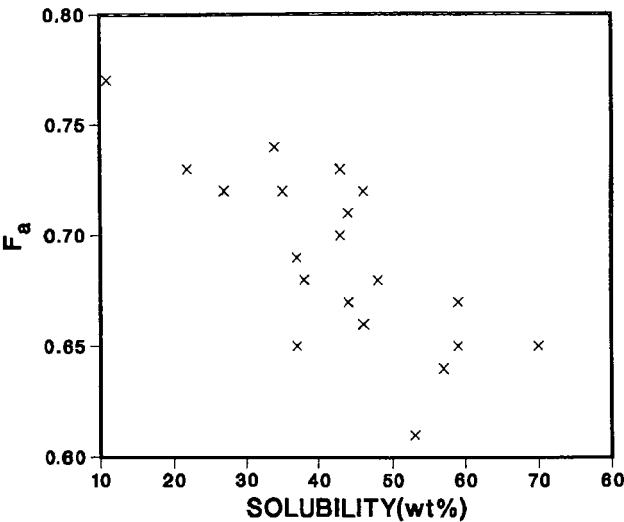


Figure 6. Variation of fa with benzene-ethanol solubility for the Exxon coals.



CHANGES IN HYDROGEN UTILIZATION WITH TEMPERATURE DURING DIRECT COAL LIQUEFACTION

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INTRODUCTION

The role of hydrogen is of particular interest in direct coal-conversion chemistry. The presence of high pressure gaseous hydrogen is beneficial in virtually any direct conversion experiment, even under low severity conditions where the net hydrogen incorporation is nil. The hydrogen chemistry is extremely important in process design due to the large impact of hydrogen consumption on the process economics. An ideal process would consume a minimum of hydrogen while breaking the coal into soluble fragments. A reliable means of monitoring the major pathways of hydrogen utilization, in contrast to only measuring net hydrogen consumption, would be very useful for process optimization. The goal of this work was to develop an analytical approach for quantitatively distinguishing hydrogen consumed in hydrogenation from that utilized to stabilize thermolysis fragments.

The current view on the involvement of hydrogen in coal liquefaction is that it is consumed in direct hydrogenation and in the "capping" of thermolysis fragments.¹ In the capping mode, the hydrogen may be transferred by means of solvent intermediates such as hydroaromatics. The direct hydrogenation of aromatics is reasonably well understood, but the mechanism of hydrogen transfer is less clear. Upon homolytic thermolysis of a labile bond in the feed slurry, two free radicals are formed, which then stabilize by abstraction of hydrogen from nearby groups, by rearrangement, or by coupling. Rearrangement and coupling reactions of radicals can often result in hydrogen being eliminated from the fragment rather than consumed by it. In the complex, high molecular weight, slurry environment, all these routes to radical stabilization are accessible.

If coals were simple solid hydrocarbons (C_xH_y) without mineral matter or heteroatoms, there would be little interest in liquefaction, since a major goal of liquefaction is the removal of N, O, S, and mineral matter from the coal. Heteroatom removal is one of the most important roles for hydrogen in coal liquefaction, and it can be considered a subcategory of the thermolysis stabilization reactions just described.

Experimental evidence shows that the simple picture of bond thermolysis/radical stabilization outlined above is a gross oversimplification of direct coal conversion chemistry. In liquefaction experiments under an atmosphere of deuterium, the label is found in virtually all positions in the product. Positions α to aromatic rings are usually preferred, but a significant portion of the label appears in aromatic positions.² The methane produced also contains significant concentrations of deuterium, and dideuteromethane often predominates.³ The presence of coal strongly catalyzes isotopic scrambling in a number of model systems.⁴ These results are difficult to rationalize using the very simple model for hydrogen utilization.

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

Also, considerable conversion of coal to soluble products can occur under mild conditions where no net hydrogen is consumed. In this case, any hydrogen consumed must be compensated for within the slurry system. The ability of coal to act as a hydrogen donor is well documented.⁵

In a realistic direct conversion process, the distinction between coal and solvent is somewhat artificial. The slurry vehicle in a continuous unit operating at a steady state is a subfraction of the product from a previous cycle, making it impossible to clearly distinguish "solvent" from product oil in the reactor effluent. There is substantial evidence that solvent quality is enhanced by inclusion of certain high molecular weight components.⁶ The solvent in these systems is intimately involved as a reactant and not as a neutral diluent. Thus, it may be preferable to consider the total feed slurry as a reactant mixture rather than as coal plus solvent.

Formulation of Analytical Approach

The fact that it is difficult to understand the detailed, molecular-level mechanism of hydrogen incorporation in complex liquefaction systems does not preclude improvements in understanding the net chemistry. It is reasonable to assume that hydrogen consumption will involve either hydrogenation or bond scission reactions. Conversely, both aromatization, the reverse of hydrogenation, and condensation, the reverse of bond scission, are potential sources of hydrogen. Exchange and isomerization reactions do not affect the net hydrogen balance.

Since stoichiometries of the two classes of hydrogen incorporation reactions differ, it is possible to construct a model that discriminates between the two. Such a model requires determination of the change in total hydrogen, the change in aromatic hydrogen, and the number of hydrogens incorporated during bond cleavage. The relationship between these quantities will be expressed as

$$\Delta_{\text{Total}}^{\text{H}} = \Delta_{\text{Cleavage}}^{\text{H}} + \Delta_{\text{HYD}}^{\text{H}} \quad (1)$$

where $\Delta_{\text{Total}}^{\text{H}}$ is the total change in hydrogen,

$\Delta_{\text{Cleavage}}^{\text{H}}$ is the hydrogen consumed in bond cleavage, and

$\Delta_{\text{HYD}}^{\text{H}}$ is the hydrogen consumed in hydrogenation of the slurry.

This relationship describes only the reactions of hydrogen with the organic portion of the feed slurry. Focusing attention only on the organic reactions alleviates, to some extent, problems in the interpretation of total hydrogen balances. In total hydrogen balance calculations, it is impossible to distinguish H_2S and H_2O arising from organic reactions from those produced by inorganic sources in the coal. Although NH_3 presents less of a problem, some ammonia may be liberated from certain clays upon heating. The analytical problems associated with measuring small changes in the huge excess of gaseous hydrogen normally present under direct conversion conditions are also eliminated, since only carbonaceous products are analyzed.

Assuming that the total change in hydrogen ($\Delta_{\text{Total}}^{\text{H}}$) can be determined by classical elemental analysis, then a method for measuring either the hydrogen consumed upon hydrogenation or bond cleavage is needed to use Equation 1. Since no satis-

factory method is available to count bonds before and after reaction in a coal liquefaction system, it is necessary to concentrate on determination of $\Delta_{\text{H}}^{\text{H}}_{\text{hyd}}$. Although research efforts are underway to determine hydrogen speciation in solid coals, it is doubtful that any of the current methods are sufficiently quantitative for the present purpose.⁷ One analytical tool that can be applied with reasonable confidence to both solids and liquids is ^{13}C nuclear magnetic resonance (NMR). Fortunately, it provides an indirect measurement of the hydrogen consumed in hydrogenation. Hydrogenation of organics results in incorporation of one hydrogen for every carbon reduced. Thus if a sample is hydrogenated without structural changes from an aromaticity of 0.80 to 0.70, then 10 carbons per 100 have been reduced and 10 hydrogens have been incorporated. The ratio of 1 hydrogen per carbon reduced does not hold exactly if there is significant reduction of aromatic nitrogen heterocycles, but the 1:1 stoichiometry is a good approximation if these reactions can be neglected. Combining elemental analysis and ^{13}C NMR data, the amount of hydrogen consumed in bond scission can be determined by difference.

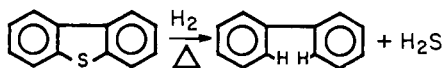
Bond scission can be further divided into three categories, those resulting in (1) heteroatom elimination as H_2O , H_2S , or NH_3 , (2) $\text{C}_1\text{-C}_4$ hydrocarbon gas production, and (3) breakdown of the coal matrix to yield nonvolatile (solid or liquid) products.

$$\Delta_{\text{Cleavage}}^{\text{H}} = \Delta_{\text{NOS}}^{\text{H}} + \Delta_{\text{C}_1\text{-C}_4}^{\text{H}} + \Delta_{\text{Matrix}}^{\text{H}} \quad (2)$$

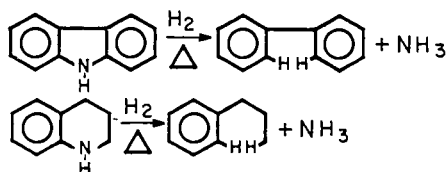
If a quantitative measure of the hydrogen used in these three bond scission modes can be obtained, it would be very useful in monitoring changes in liquefaction chemistry with reactor conditions such as temperature, pressure, catalyst, residence time, and feed composition.

In many respects, the direct conversion reactor is an inefficient coal gasifier that converts 5-20% of the coal to $\text{C}_1\text{-C}_4$ hydrocarbons while producing a by-product liquid (20-80%). Since $\text{C}_1\text{-C}_4$ hydrocarbon gases usually constitute a significant product stream, they must be carefully analyzed if the approach just described is to succeed. If accurate gas analyses are available and it is assumed that all hydrocarbon gases are generated by cleavage of alkyl substituents from aromatics, an estimate of the hydrogen consumed in gas production can be obtained. One mole of hydrogen is incorporated for every mole of light gas formed.

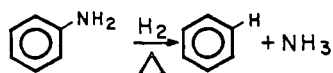
The most difficult term to evaluate in Equation 2 is $\Delta_{\text{NOS}}^{\text{H}}$, the hydrogen consumed in heteroatom removal. The difficulty arises because of the variety of heteroatomic structures present and the different hydrogen stoichiometries involved in their elimination. If the organic sulfur in the feed slurry can be assumed to be primarily thiophenic, two hydrogens are incorporated per sulfur removed as H_2S :



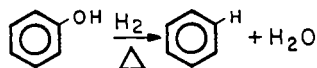
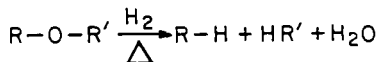
Removal of heterocyclic nitrogen proceeds through the fully hydrogenated nitrogenous ring system (5- or 6-membered).⁸ There is a net incorporation of one hydrogen per nitrogen eliminated:



If amine functions exist in the feed, elimination of one amine nitrogen actually decreases the hydrogen content by one hydrogen:



If the discussion is confined to bituminous coals, the majority of the organic oxygen will reside in either phenolic or ether structures.⁹ Removal of ether oxygen results in the net incorporation of two hydrogens per oxygen removed, and removal of phenolic oxygen results in no net change in hydrogen:



Under mild conditions where only minimal heteroatom removal occurs, the question of hydrogen stoichiometry is unimportant. However, under severe processing conditions significant heteroatom reduction can occur and an average stoichiometry must be assigned. For the present purposes, it has simply been assumed that on the average one hydrogen is incorporated into the carbonaceous product per heteroatom removed from the organic portion of the feed slurry.

Combining Equations 1 and 2 yields

$$A_{\text{Total}}^{\text{H}} = A_{\text{HYD}}^{\text{H}} + A_{\text{C1-C4}}^{\text{H}} + A_{\text{NOS}}^{\text{H}} + A_{\text{Matrix}}^{\text{H}} \quad (3)$$

The term $A_{\text{Matrix}}^{\text{H}}$ can be determined by difference. Using Equation 3, only elemental analyses, carbon aromaticities, and quantitative gas analyses are required to partition the hydrogen consumption into that used in gas production, hydrogenation, heteroatom removal, and matrix bond cleavage. In reactions producing significant CO or CO₂, a correction must be applied to Equation 3, but in the experiments described below, both CO and CO₂ were negligible.

Experimental

The model just described was initially applied to a single steady-state period 800 hours into a long-term liquefaction experiment (FB-62) on the 400 lb/day coal liquefaction unit at PETC.¹⁰ The unit was operated at 450°C under 4,000 psig H₂ pressure while feeding a 35% slurry of West Virginia (Ireland Mine) HvAb coal in centrifuged liquid product from a previous period of the run. Subsequently, a series of liquefaction runs on a 10 lb/day continuous coal liquefaction unit at PETC was investigated.¹¹ In the latter unit, a 40% coal slurry prepared from Homestead, Kentucky, HvAb coal and centrifuged liquid product produced from the same coal in the 400 lb/day unit was liquefied under 2000 psig H₂ at programmed temperatures between 375°C and 450°C. More recently, two series of experiments have been studied involving liquefaction of reactive (Illinois No. 6) and refractory (Blacksville No. 2) coals in the presence of SRC-II distillate in a stirred autoclave under 2000 psig H₂ over the temperature range 300°C to 450°C.

Elemental analyses of the organic material in the feed slurries were obtained from separate analyses of the vehicles and coal. Elemental analyses of the vehicles were done by classical microanalytical procedures, including direct oxygen determinations. The feed coals were analyzed by both microanalytical and standard

ASTM coal methods for moisture, ash, and sulfur forms. Product gases were analyzed by low resolution mass spectrometry of grab samples and gas chromatography. The products were split by Soxhlet extractions into methylene chloride soluble and insoluble fractions, which were then analyzed separately. The carbon aromaticity change across the reactor was determined by ^{13}C NMR, using the CP/MAS technique on the insoluble fractions and high resolution ^{13}C NMR in CD_2Cl_2 for the soluble fractions.

Results and Discussion

A comparison of the net changes in composition of the feed slurry and total product for Run FB-62 on the 400 lb/day unit is presented in Table 1. Combined with the gas make (8 wt% maf), the data in Table 1 allow application of Equation 3 to determine the modes of net hydrogen utilization in the reactor shown in Table 2.

Table 1. Analysis of feed slurry and total product, Run FB-62.

	Elemental Analyses (atoms/100 carbon atoms)					Carbon Aromaticity (f_a)
	C	H	N	O	S	
Feed Slurry	100	96	1.3	4.3	0.8	0.70
Total Product	100	106	1.3	2.6	0.6	0.67
Net Change	---	+10	0	-1.7	-.2	-0.03

Table 2. Net hydrogen utilization in Run FB-62.

Mode of Hydrogen Utilization	H Consumed/100 C
Gas Make	2
Heteroatom Elimination	2
Hydrogenation	3
Matrix Cleavage	3
Total	10

The results indicate nearly equal consumption of hydrogen by each of the four pathways considered at 450°C in the 400 lb/day unit.

Products produced at various temperatures in the 10 lb/day unit were then analyzed to determine if this analytical approach would detect changes in hydrogen utilization as reactor conditions changed. A plot of total product aromaticity vs. programmed reactor temperature is shown in Figure 1. The actual reactor temperatures vary somewhat from the programmed temperatures, but for simplicity, Figure 1 uses the programmed temperature. The three data points at each temperature correspond to three different hydrogen flow rates (80, 103, and 125 SCF/hr). The spread in values at a given temperature arises from experimental errors in the f_a determination and from sampling errors, as well as any real effect of hydrogen flow rate. Current work is being directed toward reduction of the data scatter. In this work the data points are all presented with no statistical justification of the indicated curve. Since other analyses show little, if any, effect of hydrogen flow rate in this range, the f_a values at each temperature can be averaged to yield an estimate of the actual best value indicated on the plot as a star.

The horizontal dashed line in Figure 1 indicates the carbon aromaticity of the slurry feed, obtained as a weighted average of the aromaticities of the slurry components. At low temperatures, where no chemical reaction takes place, the reactor would simply be mixing the slurry components. At the other extreme in temperature (450°C), the liquid product aromaticity is expected to again approximate the value for the solvent, since this is a requirement for steady-state recycle operation. Figure 1 indicates that the total aromaticity has nearly returned to the slurry line at 450°C, and the liquid product (CH₂Cl₂ solubles) has an aromaticity (0.69) that compares well with that of the vehicle (0.68). The most distinctive and surprising feature in Figure 1 is the apparent minimum in the carbon aromaticity at 400°C. This minimum suggests very significant changes in product hydrogen distribution upon going from 375°C to 400°C. This change is observed, although there is still little net hydrogen incorporation, no gas production, and relatively little heteroatom elimination at these temperatures. The only heteroatom lost under these conditions is oxygen, and part of this apparent loss may well be due to simple water loss rather than elimination of organic oxygen.

Applying the model to the average f_a data in Figure 1 results in the hydrogen utilization pattern shown in Table 3. As anticipated, little net hydrogen chemistry has occurred at 375°C. The only directly measurable change is the loss of one oxygen atom per 100 carbon atoms, requiring one hydrogen from matrix bond formation for balance. At 450°C, a hydrogen utilization profile much like that observed for Run FB-62 in Table 3 would be expected, and in general, that is what is found. The only difference is that the net hydrogenation is apparently less in the smaller 10 lb/day reactor that was operated at the lower hydrogen pressure. The term "apparently" should be stressed, since the absolute accuracy of f_a measurements on such samples is probably no better than ± 0.03 . At 400°C, Table 3 indicates a significantly higher consumption of hydrogen by hydrogenation, 7 hydrogens/100 carbons, while the total net hydrogen incorporation is only 3 hydrogens/100 carbons. Since 2 hydrogens/100 carbons are consumed in heteroatom removal, this indirect analysis indicates consumption of 9 hydrogens/100 carbons in the 400°C slurry, while elemental analysis indicates an incorporation of only 3 hydrogens/100 carbons overall. The model then forces assignment of a negative value to matrix cleavage consumption, implying that the net change in number of bonds across the reactor is an increase. This suggests that under these conditions, internal condensation of the slurry components is producing hydrogen that compensates for that consumed in bond cleavage, heteroatom removal, and hydrogenation. It must be emphasized that this treatment considers only net chemistry, making it impossible to determine if the internally produced hydrogen or the hydrogen atmosphere provides the consumed hydrogen.

Table 3. Hydrogen utilization during liquefaction of Homestead, Kentucky, coal in the 10 lb/day unit.

Mode of Hydrogen Consumption	Hydrogens Consumed Per 100 Carbons in Feed		
	375°C	400°C	450°C
Gas Make	0	0	4
Heteroatom Removal	1	2	4
Hydrogenation	0	7	1
Matrix Cleavage	-1	-6	3
Total	0	3	12

Table 3 indicates that as the temperature of the reactor increases from 400°C to 450°C, the total hydrogen incorporation per 100 carbon atoms increases dramatically from 3 to 12, but the net consumption in hydrogenation actually decreases from 7 to 1. This effect is probably due to increasing hydrogen production via

aromatization with increasing temperature. This is not unexpected, since low temperatures tend to favor hydrogenation, while high temperatures favor aromatization. Higher temperatures also tend to favor thermolysis over hydrogenation, and this expectation is also confirmed in Table 3, where the net bond-breaking consumption (gas make, heteroatom removal, and matrix cleavage) changes from -4 hydrogens/100 carbons at 400°C to +11 hydrogens/100 carbons at 450°C. However, even at 450°C, only 3 hydrogens/100 carbons are consumed in breaking down the slurry matrix bonds. This indicates that bond breaking predominates over condensation by only about 1.5 bonds/100 carbons.

Using the approach outlined, a reasonable picture of the changes in hydrogen utilization with temperature emerges. At low temperature (375°C), physical changes and minor internal hydrogen redistribution occur with little net hydrogen chemistry and no net consumption. At 400°C, there is still only a small hydrogen consumption, but there is also evidence of significant internal hydrogen chemistry, with hydrogenation and condensation proceeding to approximately the same degree. At high liquefaction temperatures, a more conventional view of hydrogen utilization emerges, significant net consumption being utilized primarily in bond cleavage reactions, gas make, heteroatom removal, and matrix breakdown.

An additional series of autoclave experiments on the liquefaction of Illinois No. 6 and Blacksville No. 2 coals is currently being investigated to determine if this approach can distinguish differences in hydrogen utilization between coals of different reactivity over the temperature range 300°C to 450°C. Although analyses of these runs are not yet complete, preliminary results indicate there are distinct differences between the coals in the product aromaticity versus temperature relationship.

Although the approach presented appears to be useful on the basis of the results accumulated to date, a discussion of potential problems is appropriate. Analytical errors associated with the various measurements and the assumptions of the model both contribute to uncertainty in the results. The NMR determination of f_a is a prime source of error. For this number to have any utility, all the feed and product carbons must be observed and carefully quantified. The problem of observing all of the carbon in the soluble material is not too serious if the "soluble" material is not colloidal or suspended. If the correct NMR parameters are used, the largest source of error is then in the integration of peak areas. The problem of quantitatively determining f_a for the insoluble fractions, which requires the ^{13}C -CP NMR technique, is more serious. This technique will not observe liquid-like entrapped material and may not observe carbons that are too far removed from hydrogen for the efficient transfer of polarization. The lower inherent resolution of the solid phase NMR spectra also introduces a larger error in measurement of overlapping peak areas. Another potential source of error is the quantitative determination of gas yield and composition. This measurement is important due to its large impact on both total hydrogen consumption and net product aromaticity. The determination of organic oxygen in coal and coal-derived products is always a problem, and errors in this determination translate directly into errors in hydrogen in heteroatom removal. The determination of organic sulfur in the feed slurry requires distinguishing between organic and mineral sulfur in the coal.

Conclusions

The approach outlined yields a rather detailed description of the net utilization of hydrogen during direct liquefaction, partitioning it into contributions from gas generation, heteroatom removal, hydrogenation, and matrix breakdown. Preliminary results indicate that internal hydrogen reorganization, with little consumption, predominates at low temperatures, with hydrogenation being compensated for by the hydrogen liberated in condensations. As the temperature is increased, bond cleavage reactions and aromatization reactions appear to become more important,

and the net hydrogen consumption increases. Additional studies of the assumptions in the model and of uncertainties in the required analytical data are needed to critically evaluate the utility of this approach.

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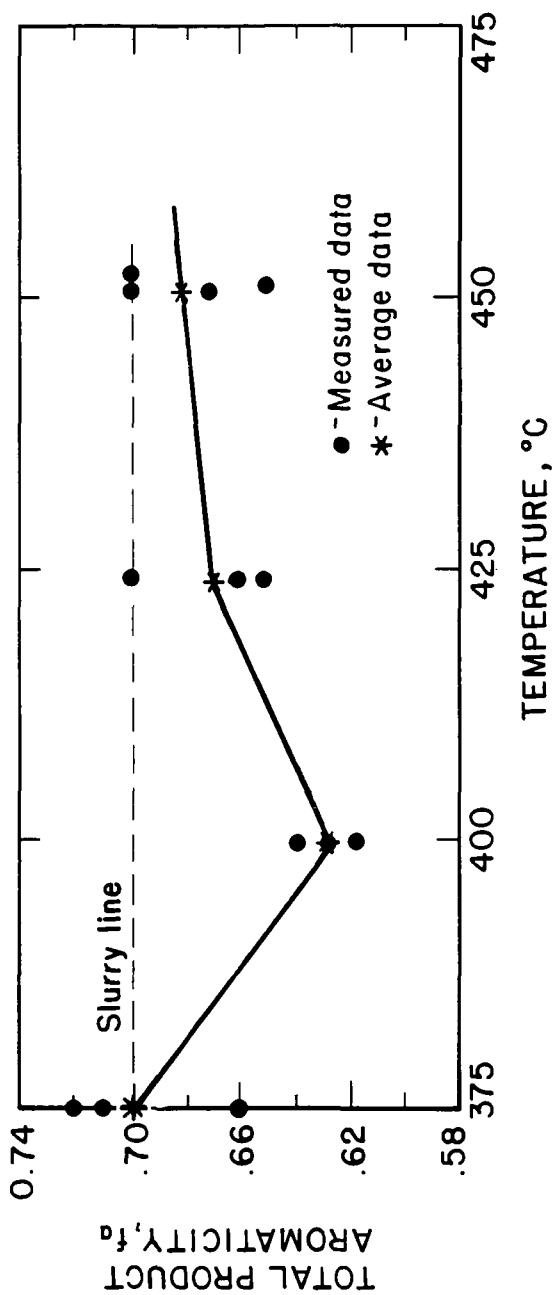


Figure 1 - Dependence of total product aromaticity on temperature.

CHARACTERIZATION OF ARTIFACTS PRODUCED
FROM TETRALIN DONOR VEHICLE UNDER
COAL LIQUEFACTION CONDITIONS

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ABSTRACT

The hexane-soluble oil fraction of the heavy liquids produced from the liquefaction of coal using tetralin donor vehicle was fractionated by high pressure liquid chromatography. Three fractions were obtained: saturates, aromatics and polars. Each fraction was individually characterized via capillary column gas chromatography/mass spectrometry. Several binaphthyls and binaphthyl derivatives, produced from the donor solvent tetralin under coal liquefaction conditions, were identified in the aromatic fraction. These artifacts make up an important fraction of the whole aromatic fraction. There is a fairly clear tendency for the concentration of binaphthyls and derivatives to decrease with increasing rank of coal. A stepwise multiple regression analysis shows that the clay minerals and pyrite present in coal independently catalyze one or more of the types of artifact formation.

INTRODUCTION

Partially hydrogenated aromatic solvents such as tetralin, hydrophenanthrenes and hydropyrenes are used as process solvents in several coal liquefaction processes. An important function of these solvents is to donate hydrogen necessary for capping the thermally produced free radicals from coal thereby preventing char formation. The effect of hydrogen donor concentration on the conversion of coal to THF or pyridine-soluble products has been thoroughly investigated (1,2) and several modern analytical techniques have been applied to characterize the ensuing products of liquefaction. Combined gas chromatography-mass spectrometry (GC/MS) has been extensively used in the characterization of liquefaction products from coal conversion processes (3-6). However, only a limited amount of work has been done on the identification of artifacts produced from the donor solvent itself under the coal liquefaction conditions (7-9). A knowledge of the artifacts generated from the process solvent will be very helpful in developing methods for down-stream processing of the coal-derived liquids. In this paper, we describe the identification of the artifacts produced from a process using tetralin as the hydrogen-donor solvent for liquefaction of coal and the influence of coal characteristics on the concentration of the artifacts is also discussed.

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EXPERIMENTAL

Coal Samples:

Selected characteristics of the coals used in the liquefaction studies are shown in Table 1. The set of coals covers a wide range of rank and geologic province; the mineral matter content varies from a low of 6% to a high of 34% and a wide variation in the sulfur content can also be noted. Other characteristics of the coals, such as macerals content, calorific value, composition of the mineral matter are available from the Penn State/DoE coal data base. The aromaticities were determined by Gerstein, et al. using CP-MAS ^{13}C nmr (10).

Liquefaction:

The liquefaction runs were performed in duplicate in tubing bombs under the following conditions: 2.5 gm coal + 7 ml tetralin, 425°C, H_2 pressure (at temperature) 1400 psi, 30 min reaction period and agitation at 400 min^{-1} . After the gases had been vented, the products were rinsed out of the reactor into a Soxhlet thimble with ethyl acetate. Extraction was continued in the Soxhlet apparatus for 24 hours. After evaporation of the ethyl acetate, the residue was weighed to determine the total conversion and then mixed with 500 ml hexane and left to stand overnight, after which it was filtered. After removal of the hexane, the soluble portion was distilled at about 70°C and 5 mm Hg pressure to remove naphthalene and excess tetralin and the monomeric by-products formed from them during the process. The undistilled material was weighed and is reported as "oil".

Analytical Procedures:

i) HPLC Separation:

Prior to GC/MS analysis, group type separation of the hexane-soluble oil was performed using a Waters Model ALC/GPC-201 HPLC (Waters Associates, Milford, Mass.). The instrument contained of the following accessory hardware: Model 6000A solvent delivery system, a Model 660 solvent programmer, a Model U6K septumless injection system, a Rheodyne Model 7010 backflush valve and a Model 440 absorbance detector with inter-changeable UV filters.

Typically, 20 microliter of the oil was injected on to a semi-preparative (8mm ID X 30 cm length) micro-Bondapak- NH_2 column (Waters Associates, Milford, MA.). The mobile phase was spectral quality n-hexane distilled in glass (Burdick and Jackson, Muskegon, MI) and a flow rate of 6.0 ml min^{-1} was used. Saturates are not retained in the column and are eluted first followed by aromatic hydrocarbons. Polars have greater affinity towards the stationary phase which makes the analysis time longer. Hence after the elution of the aromatic hydrocarbons, solvent flow through the column was reversed using the backflush valve and the eluting material was collected as the polar fraction. UV detector response at 254 nm was recorded for the aromatic and polar fractions.

The three fractions--saturate, aromatic and polar--were collected in separate flasks and excess hexane from the fractions was distilled off in a rotary evaporator. Further concentration was effected by blowing a gentle stream of nitrogen using a Sillivap concentrator.

ii) GC/MS Characterization:

Identifications of individual components in each fraction were performed on an integrated GC/MS/Computer system. The instrument used was a Finnigan Model 4000 automated EI/CI mass spectrometer equipped with a quadrupole ion detector and interfaced with a Finnigan Model 9610 gas chromatograph and a dedicated LSI computer with 16K memory.

Several stationary phases coated on glass capillary columns were tested for their application which included SP-2100, SP-2250 (both from Supelco Inc., Bellefonte, Pa.), SE-30, SE-52, SE-54 and Dexsil 300 (all from Applied Science Lab., State College, Pa.). A 30 meter SE-54 (methylphenylsilicone) stationary phase coated-glass capillary column (film thickness, 0.25 micrometer) was found satisfactory for the analyses of both aromatic and polar fractions.

The operating conditions used for the GC were: injector temperature 250°C; carrier gas, helium; flow-rate, 1 ml/min. The sample was quantitatively introduced into the capillary column by purged splitless injection technique (11). The oven temperature was initially programmed to increase from 50° to 100°C at 20°C min⁻¹ and then to 300°C at 5°C min⁻¹.

The mass spectrometer was operated in the electron-impact mode (70eV electron energy). Chemical ionization mass spectra (methane reagent gas) of the eluting components were obtained when necessary. Spectral data acquisition was performed at appropriate scanning intervals and the mass spectra were recorded on magnetic tapes for later retrieval. Specific compound identification was made from the characteristic mass spectral splitting patterns. Retention time data and response factors were obtained for representative compounds. By monitoring the specific ion current (single ion monitoring), detection of compounds present at trace levels was considerably improved.

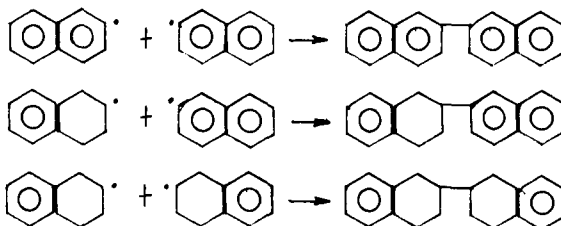
RESULTS AND DISCUSSION

Tetralin has been widely used as a hydrogen donor solvent in many coal liquefaction studies. In addition to the transfer of hydrogen from the hydroaromatic ring to coal free radicals, tetralin undergoes the following changes under coal liquefaction conditions:

1. Isomerization: Tetralin rearranges (isomerizes) to produce methylindans. This reaction is temperature dependent (12) and is catalyzed by pyrite (13).

2. Fragmentation: In this case, tetralin decomposes to produce a mix of smaller molecules which is mainly made up of alkylbenzenes. Curran et al. reported that the decomposition of tetralin to C₄ benzenes was enhanced in the presence of coal extracts (14).

3. Addition/Polymerization: From deuterium labelling studies, Franz et al. showed that both 2-tetralyl and 1-tetralyl radicals are produced in competitive amounts when a low-rank coal is heated in tetralin (15). The tetralyl or naphthyl radical intermediates can react with free radicals generated from coal or they can recombine among themselves leading to polymerized products such as binaphthyls and their derivatives.



Various other isomers of the above representative compounds are also possible.

On the basis of their results from the flash pyrolysis of 1- and 2-tetralyl radical precursors in vacuum, the above authors suggested that the hydroaromatic radical intermediates 'may prefer disproportionation over combination pathways as temperatures increase'. While this is true for pyrolysis experiments at high temperatures and short residence times, it can not be generalized for coal liquefaction experiments at intermediate temperatures (400-450°C) and considerably long residence times (ca. 30 min.). Our results indicate that the dimerization of solvent radical intermediates occurs to a significant extent in a coal-tetralin system and that the concentration of the resulting artifacts seems to be affected by the coal characteristics.

A representative HPLC separation of an oil product is shown in Figure 1. Figure 2 shows the reconstructed Total Ion Chromatogram (TIC) of the aromatic fraction of the oil from PSOC-739. The large peaks at scan numbers 370 to 410 in the TIC in figure 2 are due to binaphthyls and related compounds, which evidently make up an important fraction by weight of the whole aromatic fraction. Similar results were obtained with other coals. Figure 3 shows the Specific Ion Chromatograms (SIC) for m/e values of 254, 258 and 262 corresponding to the molecular ions of binaphthyl and its tetrahydro and octahydro derivatives. The peaks are numbered and identified by number in Table 2. It will be seen that, in peak height, 2,2'-binaphthyl and its derivatives predominate, indicating the higher reactivity of the 2-position compared to that of the 1-position.

When all the peaks are examined at the same attenuation, it is seen that binaphthyls and hydrogenated derivatives account for over 70% of the dimeric artifacts formed in the hydrogenation of all coals but that of highest rank, PSOC-801 (Stigler seam, Oklahoma). Having regard to the small size of other peaks in the TIC, it is unlikely that binaphthyls generated from the coals account for much of the peak heights observed. Philip et al. reported the presence of two isomers of octahydrobinaphthyls in a sample from the liquefaction of a Texas lignite using tetralin as the hydrogen-donor solvent (16). The actual amount of these and other products, however, was not specified. Schultz et al. identified 2,2'-binaphthyl (only) among the aromatic hydrocarbons in a SRC pilot plant product with a mixture of Kentucky Nos. 9 and 14 coals as feedstock, but only in trace amount (6). Thus the binaphthyls found in our work are indeed very largely artifacts of the solvent. In what follows, all of the compounds named are assumed to be derived entirely from the solvent.

In addition to the binaphthyls discussed, a number of phenyl naphthalene were identified: C₁-, C₂- and C₄-phenyl naphthalenes, and a phenyl tetralin. Only the sum of these compounds are shown in Table 3, under the heading $\Sigma\phi-v$. Furthermore, a number of alkyl naphthalenes and either alkyl indans or alkyl tetralins (or a mixture) were found (C₁-C₄). Again, only the sum of the concentrations of these compounds is shown in Table 3, under the heading ΣC_n-v . The part of the HPLC fraction 2 (aromatics) accounted for by solvent artifacts is shown as a percentage in the final column of Table 3.

There is a fairly clear tendency for the concentration of binaphthyls and derivatives to decrease with increasing rank. The concentration of phenyl naphthalenes, whose formation involves ring-splitting, tends to increase with rank, as does the concentration of alkyl naphthalene/indan derivatives, whose formation involves isomerization. As mentioned before, the isomerization of tetralin to methyl indans is catalyzed by pyrite (13); yet there is no correlation between the concentration of these derivatives and pyrite content. In fact, it is reasonable to suppose that many factors determine the yields of the various kinds of artifacts. This is substantiated by an equation developed by stepwise multiple regression:

$$\text{Concentration of artifacts (\%)} = 0.919 \text{ MM} + 14.5 \text{ S}_{\text{pyr}} - 9.81 f_a + 38.2$$

The variables provided for the regression were: contents of C, O, S_p, S_{tot} and MM, and the aromaticity, f_a. The fraction of variance explained by this regression, R², is 0.851. The equation suggests that both clay minerals and pyrite independently catalyze one or more of the types of artifact formation. Abdel-Baset (13) found that clay minerals catalyze transfer of hydrogen from hydroaromatics to aromatics. Thus the significance of f_a in the equation may lie in the fact that it indicates the number of C atoms available for accepting H atoms and hence (presumably) for generating free radicals in the solvent (admittedly this term may be not very significant since the range of values of f_a is small).

In comparing the yields and composition of the products of liquefaction experiments, it might be considered desirable to subtract out the components derived from the solvent. The aromatic fraction of the oil (HPLC fraction 2) can be corrected as follows:

$$\% \text{ aromatics (corr.)} = \% \text{ aromatics (HPLC)} \times \frac{100 - \% \text{ artifacts}}{100}$$

Consequential changes are needed in other figures characterizing the product distribution. Thus:

$$\begin{aligned} \% \text{ hexane-sol. oil (corr)} &= \% \text{ sat.} + \% \text{ arom. (corr.)} + \% \text{ polars} \\ \% \text{ benzene-sol. total liquids (corr.)} &= \% \text{ oil (corr.)} + \% \text{ asph.} \\ \% \text{ gases (corr.)} &= \% \text{ conversion} - \% \text{ total liquids (corr.)} \end{aligned}$$

The corrected and uncorrected yields of various fractions obtained from the liquefaction of coals listed in Table 1 are shown in Table 4. From the table, it is clear that the adjustment of the figures for hexane-soluble oils and for the aromatic HPLC fraction makes a quite appreciable difference to the data and ought to be determined before product distributions for any batch system are evaluated.

CONCLUSION

An important fraction by weight of the whole aromatic fraction of the oils obtained from the liquefaction of coal using tetralin as the hydrogen-donor solvent was made up of binaphthyls and related compounds. The concentrations of these artifacts were affected by the coal characteristics. Both clay minerals and pyrite seem to independently catalyze one or more of the types of artifact formation from tetralin. This is a somewhat unexpected effect of coal characteristics on the composition of liquefaction products. Other donor solvents, such as partially hydrogenated phenanthrene or a commercial recycle oil, are obviously likely also to undergo changes during processing, whose magnitude and nature will vary with the feedstock, and whose effects on product composition will be appreciable.

ACKNOWLEDGEMENT

The coals used in this study were kindly supplied by Dr. William Spackman, Professor of Palaeobotany and Director of the Coal Research Section in this College. This work was supported by Contract No. DE-AC22-81-ET 10587 from the U.S. Department of Energy.

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Table 1
Selected Characteristics of Coals Used

PSOC No.		Province*	ASTM Rank	% C dmmf	% S dry	% MM, [†] dry	f _a ^{**}
833	Fort Union Bed, Mont.	3	Lig	70.43	0.55	16.26	0.68
791	A Pit, Texas	6	Lig	72.13	0.81	20.78	0.55
785	Lower Wilcox, Texas	6	sbb	73.21	1.06	14.29	0.54
240A4	Big Dirty, Wash.	5	sbb	74.34	0.39	17.82	--
240A1	Big Dirty, Wash.	5	sbb	75.11	3.36	33.98	--
866	G Seam, Colo.	4	HVC	76.97	0.50	22.22	0.64
548	Wolf Creek, Colo.	4	HVC	78.98	0.52	13.11	0.64
680	Indiana No. 6, Ind.	2	HVC	80.61	3.58	14.23	--
854	Juniata C, Colo.	4	HVB	81.64	0.40	6.71	0.63
739	Kentucky No.12, Ky.	2	HVB	83.29	2.72	15.05	0.70
773	Ohio No.6, Ohio	1	HVB	83.29	2.83	9.30	0.75
808	Croweburg, Okla.	2	HVA	84.71	3.20	6.57	0.73
821	Pittsburgh, W. Va.	1	HVA	84.92	2.56	6.00	0.70
801	Stigler, Okla.	2	MV	88.35	4.65	13.83	0.79

* Key to province numbers: 1, Eastern or Appalachian; 2, Interior; 3, North Great Plains; 4, Rocky Mountain; 5, Pacific; 6, Gulf.

** Data from ¹³C nmr, kindly provided by Professor B. Gerstein, University of Iowa, now published by him (10).

† Calculated by a modification of the Parr formula (Given and Yarzab, 17).

Table 2
Identification of Peaks in Specific Ion Chromatograms
of Figure 3

Figure 3(a):	1. 1,1'-binaphthyl 2. 1,2'-binaphthyl 3. 2,2'-binaphthyl
Figure 3(b):	1. 1,2,3,4-tetrahydro-1,1'-binaphthyl 2. 1,2,1',2'-tetrahydro-2,2'-binaphthyl 3. 1,2,3,4-tetrahydro-2,2'-binaphthyl 4. 1,2,3,4-tetrahydro-2,1'-binaphthyl (three other unidentified peaks)
Figure 3(c):	1. 1,2,3,4,1',2',3',4'-octahydrobinaphthyl 2. 1,2,3,4,1',2',3',4'-octahydro-1,2'-binaphthyl 3. 1,2,3,4,1',2',3',4'-octahydro-2,2'-binaphthyl

Table 3
Concentrations of Solvent Artifacts in the
Aromatic HPLC Fraction of Some Coals

percent of total fraction

PSOC No. C	Binaphthyls	Tetrahydro- binaphthyls	Octahydro- binaphthyls	Binaphthyl derivatives (total)	$\Sigma \phi-\nu$	$\Sigma C_{H-\nu}$	Total artifacts
833	15.6	7.6	15.8	38.9	1.9	5.5	46.3
791	17.7	13.3	13.4	44.4	0.7	7.8	52.9
785	10.3	12.4	15.6	38.3	0.7	5.4	44.4
240A4	14.0	20.2	8.4	42.5	1.5	3.5	47.5
240A1	19.1	22.4	16.7	58.2	1.2	4.4	63.8
866	16.0	12.5	15.1	43.6	1.8	6.7	52.0
548	8.7	9.7	10.4	28.8	2.2	15.5	46.6
680	6.1	7.9	9.5	23.5	3.9	11.1	38.5
854	12.6	12.7	9.7	35.4	3.5	4.2	42.7
739	7.1	6.7	7.7	21.6	2.8	11.1	35.5
773	7.1	9.4	7.1	23.5	3.9	9.3	36.8
808	3.9	4.5	5.9	14.3	3.3	15.5	33.0
821	5.7	6.9	10.6	23.2	3.4	5.5	32.0
801	4.9	6.2	5.7	16.8	4.1	38.2	59.0

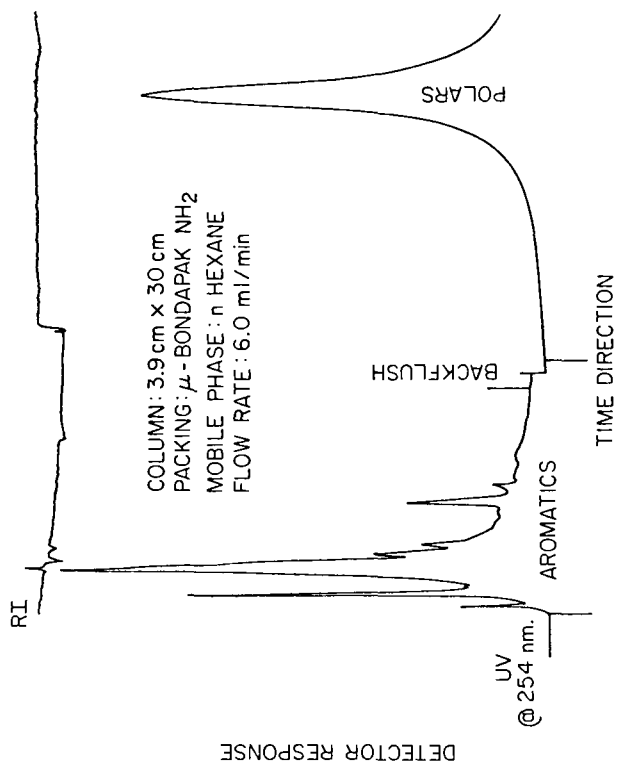
* Total phenylnaphthalenes.

** Total alkyl-tetralins and naphthalenes.

Table 4
Product Distributions from Coal Liquefaction,
Corrected for Artifacts from Solvents

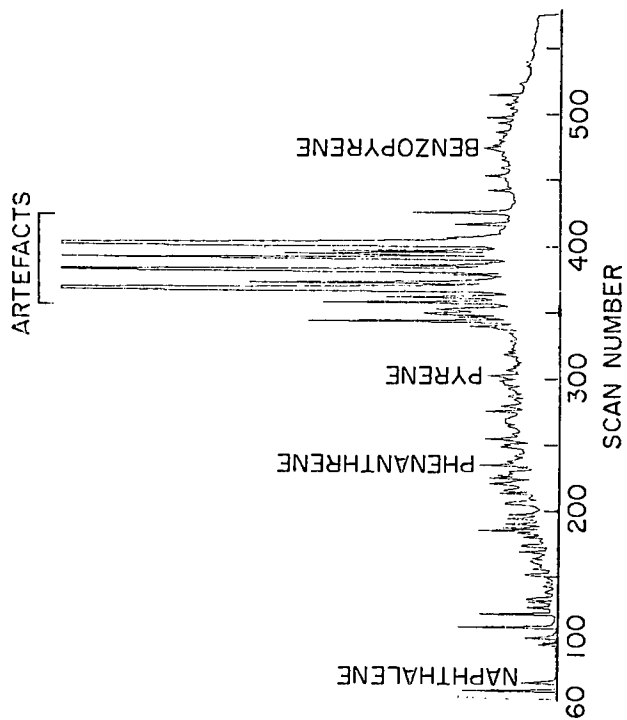
(% of dmmf coal)

PSOC No.C	Total conversion	Total liquids		Gases (by diff.)		Asphal- tenes		Hexane-sol. oil		Sat. HPLC frac.	Polar HPLC frac.	Aromatic HPLC fraction	
		uncorr.	corr.	uncorr.	corr.	uncorr.	corr.	uncorr.	corr.			uncorr.	corr.
833	50.3	28.4	24.8	21.9	25.6	16.2		10.3	8.6	0.1	6.5	3.7	2.0
791	57.8	39.7	35.6	18.1	22.2	21.4		18.4	14.3	0.2	10.4	7.8	3.7
785	57.5	38.3	34.9	19.3	22.6	21.5		16.8	13.4	0.8	8.4	7.6	4.2
240A4	59.3	38.5	35.9	20.8	23.4	25.1		13.4	10.8	0.6	7.3	5.5	2.9
240A1	70.1	45.1	40.6	25.0	29.5	22.2		18.0	13.4	0.4	10.4	7.2	2.6
866	49.1	37.3	34.7	11.8	14.4	25.7		11.6	9.0	0.2	6.3	5.2	2.5
548	52.0	42.5	39.2	9.5	12.8	24.8		17.8	14.4	0.6	9.9	7.3	3.9
680	56.9	49.3	47.1	7.6	9.8	33.3		15.9	13.8	0.1	10.1	5.8	3.6
854	53.3	44.0	42.4	9.2	10.9	31.7		12.3	10.7	0.8	7.6	4.0	2.3
739	52.0	43.6	42.0	8.4	10.0	31.4		12.3	10.7	0.9	6.8	4.6	3.0
773	55.4	47.7	46.1	7.7	9.4	35.9		11.8	10.1	0.4	6.9	4.5	2.9
808	45.4	40.2	39.0	5.2	6.4	29.2		11.0	9.8	0.3	6.8	4.0	2.7
821	58.4	52.2	50.5	6.2	7.9	39.1		13.2	11.4	0.5	7.2	5.5	3.7
801	28.5	25.0	21.3	3.6	7.3	15.7		9.3	5.5	0.3	2.7	6.2	2.5



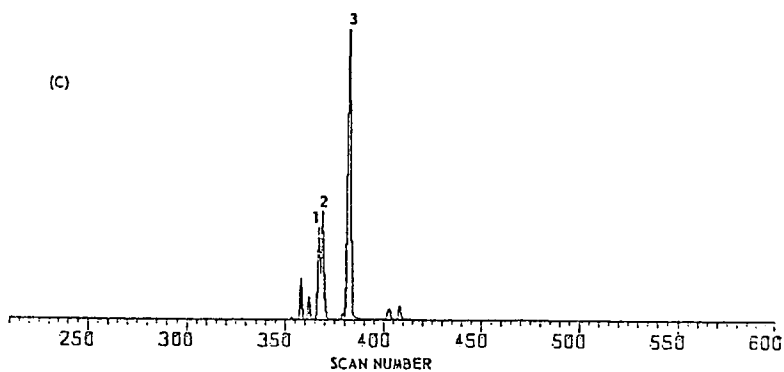
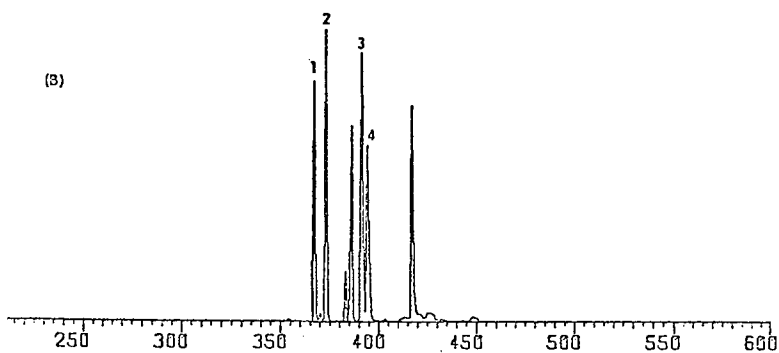
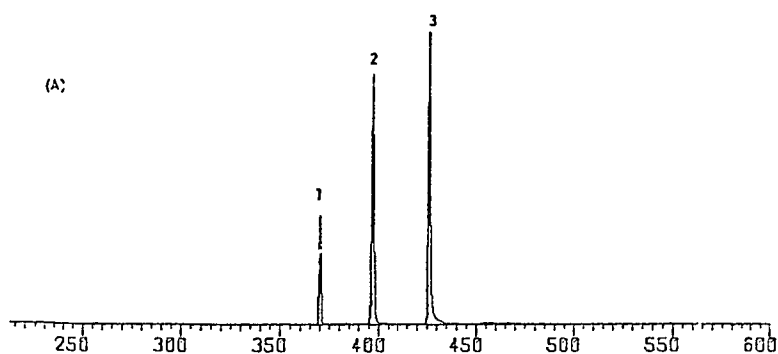
LIQUID CHROMATOGRAPHIC SEPARATION OF A VACUUM-STRIPPED OIL INTO SATURATE, AROMATIC AND POLAR FRACTIONS

Figure 1



CAPILLARY GAS CHROMATOGRAM OF AROMATIC
FRACTION FROM PSOC-739 (hvB, KENTUCKY #12)

Figure 2



Figures 3 SINGLE ION CHROMATOGRAMS FOR HPLC FRACTION 2 FROM PSOC-739 (KENTUCKY NO. 12)
(A) $m/e = 254$, (B) $m/e = 258$, (C) $m/e = 262$

FATE OF SELECTED 1-, 2-, AND 3-RING COMPOUNDS
DURING RECYCLE COAL LIQUEFACTION OPERATION

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INTRODUCTION

To observe the adduction, isomerization, and cracking of labeled solvent species, a series of coal liquefaction runs was undertaken using a bench-scale unit capable of continuous recycle operation. These experiments were made with ^{13}C -labeled solvents including octahydrophenanthrene, phenanthrene, methylphenanthrene, dimethyltetralin, and mesitylene. This work served as an extension of previously reported⁽¹⁻³⁾ laboratory-scale experiments using similar labeled model liquefaction solvents.

EXPERIMENTAL

The recycle runs with labeled compounds were performed using a continuous, bench-scale, coal liquefaction unit, a schematic of which is shown in Figure 1. In summary, the unit consisted of feed and product systems, a preheater of 8 min nominal space time, and a 1 L stirred autoclave of 60 min space time.

The operating procedure consisted of preparing a feed slurry in a heated, stirred tank separate to the unit. The feed was made up of Powhatan No. 5 Mine coal, a portion of recycle heavy product slurry from the previous period, and a process solvent generated during previous SRC-II runs in the GR&DC P-99 PDU⁽⁴⁾ feeding the same coal. The analyses of the solvent and coal are given in Table I. This feed blend was introduced into the bench-scale unit every 4 h.

The ^{13}C -labeled compounds were prepared under the direction of Professor E. J. Eisenbraun of Oklahoma State University with a portion of the analyses of intermediates and products being done at GR&DC. A detailed description of the techniques of synthesis and analyses of a portion of these compounds are reported by Seshadri et al.⁽⁵⁾ and in Reference 3.

In addition to sample distillation and routine elemental analyses, samples of heavy product slurry were Soxhlet extracted using, in sequence, the solvents: pentane, toluene, and tetrahydrofuran (THF). The Soxhlet extractions with pentane and toluene were typically of 48 h duration, and the THF of 24 h. The solvents were stripped on a steam table (80°C) with a stream of

nitrogen prior to analysis. Selected samples of separator liquids (combined No. 2, No. 3, and ice traps) and pentane solubles were separated by HPLC into saturates, aromatics, and resin (polar) fractions. An in-house HPLC was used with Bio-Sil A silica gel (20-44 micron); a description of the operating procedure was reported by Suatoni and Swab.⁽⁶⁾

The level of ^{13}C -labeling in the product fractions was determined by the standard technique of combustion to CO_2 followed by use of a Varian MAT 250 MS to determine the ratio of mass 45 to 44 (stated sensitivity of $<2 \times 10^{-6}$). Isotopic compositions are reported as values, the definition of which follows:

$$^{13}\text{C} = \frac{R_S - R_R}{R_R} \times 1000\text{‰ (parts per thousand)}$$

where R_S and R_R refer to the $^{13}\text{C}/^{12}\text{C}$ ratio in the sample and reference, respectively. The reference is PDB (Peedee Formation carbonate [belemnite]) with a value of 0.0112372. Coal has a typical range of -20 to -30 parts per million (This analysis was done at GR&DC and at Global Geochemistry Corp.)

RESULTS

Overall Material Balance of Recycle Runs--Lined-out operation of the bench-scale unit was first established with a feed consisting of Powhatan No. 5 coal, process solvent (boiling point $400^\circ\text{--}800^\circ\text{F}$), heavy recycle product slurry, and hydrogen. The product streams primarily consisted of gases, No. 2 and 3 condensates, and heavy product slurry. The reactor was run at conditions of 455°C , 1.0 h space time, and 13.8 MPa (2000 psig). After lined-out operation was achieved (34 h), a small sample of labeled octahydrophenanthrene (HPh) was introduced to the feed tank at a level of 26 g/5000 g charge. After 26 h, the next labeled compound, dimethyltetralin (DMT), was similarly charged, and the product streams were analyzed. For this and the remaining three labeled solvents, a 24-h period was used. The runs with labeled solvent were done in the following order: (89-1) octahydrophenanthrene (HPh), (89-2) dimethyltetralin (DMT), (89-3) mesitylene (MST), (89-4) methylphenanthrene (MePh), and (89-5) phenanthrene.

In all of the runs, it was assumed that the addition of the labeled solvent at a level of about 0.5 wt% once every 24 h would not affect lined-out recycle operation. Based on a detailed material balance of the second and fourth periods, this assumption appeared valid as shown in the Tables II and III.

Extraction of Process Samples from the Recycle Runs--To isolate concentrates for GC/MS and $^{13}\text{C}/^{12}\text{C}$ -MS analyses, samples of both the combined condensates and heavy slurry products were separated into fractions using extraction and HPLC. The results for 89-1 and 89-5 are given in Table IV.

Calculated Material Balance of Labeled Species--To follow the course of the ^{13}C -labeled species during SRC-II type recycle runs, it was necessary to account for both slurry product withdrawal and losses due to vaporization. In the case of very volatile compounds, most of the ^{13}C -label was recovered in the light condensate collected in the traps. This material was not recycled, and, therefore, it was quickly lost from the system. In the case of essentially nonvolatile species, losses occurred by removal of a portion of the reactor effluent stream as heavy product. To account for vaporization losses, the reactor system was modeled using average material balances with a factor "XVAP" giving the fraction of ^{13}C -labeled compound that was lost during each reactor pass due to vaporization. Figure 2 is a plot of the calculated concentration of traced (^{13}C) of the slurry from the product tank as functions of time and losses due to vaporization.

Results of Analysis of Fluids for ^{13}C -Labeled Compounds--In addition to an analysis of the product slurries and condensate streams, individual samples of pentane solubles (oils), asphaltenes, and THF insolubles were analyzed for $^{13}\text{C}/^{12}\text{C}$ ratios to determine trends with time. Overall ^{13}C material balances were calculated to show how the labeled compounds were distributed between gases, condensates (Traps 1-3), heavy products (asphaltenes, etc.), and bulk product.

As shown in Figures 3 and 4 ($^{13}\text{C}/^{12}\text{C}$ ratios of slurries and condensates), the results show the trends predicted from Figure 2. Specifically, a concentration peak occurred at about 4-6 h into the cycle, and this went essentially to zero after 24 h. In addition, the curves for the phenanthrene (Ph) and octahydrophenanthrene (HPh) runs were similar, as would be expected from the closeness of their boiling points. The loss of labeled species into the condensates recovered in the various traps also followed expected trends. As indicated by ^{13}C analysis, about 11.8% of the highest boiling labeled compound, methylphenanthrene (MePh) was found in the condensates. However, the ^{13}C -labeled methyl group readily cracked as indicated by a high recovery (namely 46.9%) of labeled gases, primarily methane. The recovery of ^{13}C -labeled compounds in the condensates from the HPh and Ph runs was essentially identical at 32.9 and 34.2%, respectively. In the run with labeled dimethyltetralin, in excess of 80% of the label was observed in the condensate. Only a low recovery (about 10%) of the low boiling mesitylene was recovered in the condensates. From an analysis of the remaining streams, it appeared that this compound was lost from the heated feed tank.

The levels of labeled compounds in the heavy product fractions somewhat follow anticipated trends. The amount of HPh held in the asphaltene fraction, by chemical adduction, was 4.8% of that fed, while that in the THF insolubles was 0.5%. In the case of Ph, the respective levels were 1.5 and 0.7%. The level of adduction of MePh was intermediate between HPh and Ph at 2.9% in the asphaltenes and 0.3% in the THF insolubles. Considering the high level of MePh cracking, these latter values are consistent with those of HPh. Essentially no adduction of dimethyltetralin and mesitylene were observed in that the $^{13}\text{C}/^{12}\text{C}$ ratios of the heavy fractions from these runs were the same as those of the base case before label use.

Reaction Trends of Individual Phenanthrene Compounds--The aromatic cuts of condensates and slurry product streams were analyzed for Run 89-1 (HPh) and 89-5 (Ph). It is first noted that octahydrophenanthrene was present in the products at concentrations less than 0.03 wt%. This compound gave up at least a portion of its hydrogen very rapidly, and, therefore, it can be considered to be absent from a recycle system unless external catalytic hydrogenation is used. Within the accuracy of the GC/MS analysis, the concentrations of phenanthrene, dihydrophenanthrene (H_2Ph), and tetrahydrophenanthrene (H_4Ph) remained essentially constant through the run periods of Runs 89-1 and 89-5. The results are given in Table V.

It is first obvious that the results from Runs 89-1 and 89-5 are consistent. The total concentrations of phenanthrene plus hydrophenanthrenes averaged 2.9 and 2.8 wt% in the condensate and slurry, respectively. (Note that alkyl substituted phenanthrenes are not included.) Due to boiling points, the relative distributions of hydrophenanthrenes to phenanthrenes were greater in the condensates than in the slurry. From an overall material balance, the conversions of coal to Ph, H_2Ph , and H_4Ph were about 0.7, 0.2, and 0.2 g/100 g MAF coal, respectively.

By a GC/MS analysis of the product fraction of Runs 89-1 and 89-5, it was found with the introduction of labeled Ph in SRC-II type operation, little of this component is hydrogenated to dihydro and tetrahydro species. In addition, an observed presence of labeled compounds of C_3 -naphthalene and isomerized derivatives of octahydrophenanthrene confirms that ring opening and isomerization of hydroaromatics occurs at coal liquefaction conditions.

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Table I

ANALYSIS OF COAL AND P-99 DERIVED PROCESS SOLVENT

<u>Sample Designation</u>	<u>Powhatan No. 5 Mine Coal</u>	<u>Process Solvent</u>
1. <u>Proximate Analysis</u>		
% Moisture	1.1	--
Ash	9.6	--
Volatile	39.6	--
Fixed Carbon	49.7	--
2. <u>Elemental Analysis</u>	(Dry)	
% Carbon	72.3	87.2
Hydrogen	5.1	8.7
Nitrogen	1.5	0.9
Oxygen	7.8 (diff)	2.8
Sulfur	3.6	0.4
Ash	9.7	--
	100.0	100.0

Table II

OVERALL MATERIAL BALANCE

Recycle Run 89

<u>Feed (g/h)</u>			<u>Products (g/h)</u>		
<u>Run Period</u>	<u>89-2</u>	<u>89-4</u>	<u>Run Period</u>	<u>89-2</u>	<u>89-4</u>
Coal	367.6	367.8	Gases (and H_2O)	98.9	97.5
Process Solvent	196.0	202.3	No. 2 Condensate	96.9	69.6
Heavy Product Slurry	661.6	656.0	No. 3 Condensate	95.1	141.8
			(plus ice traps)		
Hydrogen			Heavy Product Slurry	900.5	882.3
(Consumption)	13.9	13.7	Total	1191.4	1190.2
Total	1239.1	1239.8			
			Recovery	96.1%	96.0%

Table III

NET PRODUCT YIELDS (MAF BASIS)
Recycle Run 89

<u>Yield Component</u>	<u>89-2</u>	<u>89-4</u>	<u>Average</u>
H ₂ Consumption	-4.2	-4.2	-4.2
C ₁ -C ₄	16.5	15.7	16.1
Other Gases (CO, etc.)	2.3	2.3	2.3
Water	5.9	5.9	5.9
C ₅ -380°F	15.5	16.8	16.1
380-550°F	9.1	13.0	11.1
550-900°F	10.3	7.6	9.0
C ₅ -900°F	34.9	37.4	36.2
380-900°F	19.4	20.6	20.1
900°F+ P.S.	35.3	34.2	34.7
IOM	9.3	8.7	9.0
900°F+ Organic	44.6	42.9	43.7

Table IV

HPLC EXTRACTION SUMMARY

<u>Product Fraction</u>	<u>Saturates</u> <u>(wt%)</u>	<u>Aromatics</u> <u>(wt%)</u>	<u>Resins</u> <u>(wt%)</u>	<u>Hexane Ins.</u> <u>(wt%)</u>
<u>Run Period 89-1:</u>				
a. Condensates	5.5 ± 1.6	50.1 ± 3.8	44.0 ± 4.0	0.4 ± 0.2
b. Oils (Slurry)	2.8 ± 0.5	64.7 ± 4.1	32.5 ± 6.5	
<u>Run Period 89-5:</u>				
a. Condensates	4.8 ± 2.4	53.0 ± 5.0	41.9 ± 3.7	0.3 ± 0.2
b. Oils (Slurry)	3.3 ± 0.3	69.0 ± 3.8	27.7 ± 3.8	

Table v

SUMMARY OF PHENANTHRENE CONCENTRATIONS, WT%

<u>Component</u>	<u>89-1</u>		<u>89-5</u>	
	<u>Condensate</u>	<u>Slurry</u>	<u>Condensate</u>	<u>Slurry</u>
Phenanthrene	1.66	2.10	1.85	2.25
H ₂ Ph	0.47	0.24	0.61	0.32
H ₄ Ph	0.67	0.33	0.51	0.30
H ₈ Ph	<0.03	<0.03	<0.03	<0.03

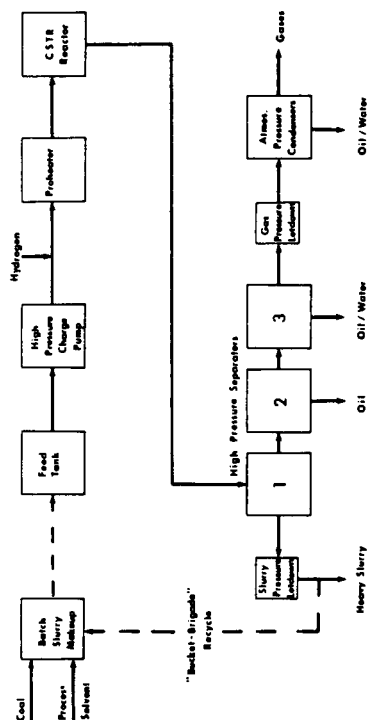


FIGURE 1: SCHEMATIC OF THE AI RECYCLE COAL LIQUEFACTION UNIT

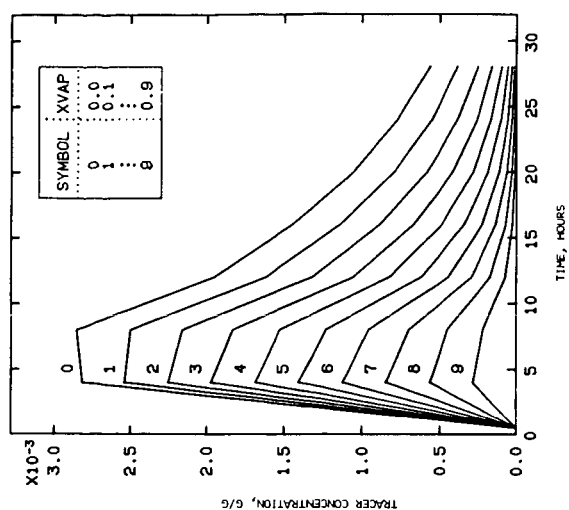


FIGURE 2: CONCENTRATION OF TRACER IN THE SLURRY PHASE AS A FUNCTION OF TIME AND FRACTION OF TRACER VAPORIZED: SLURRY DENSITY=1.00

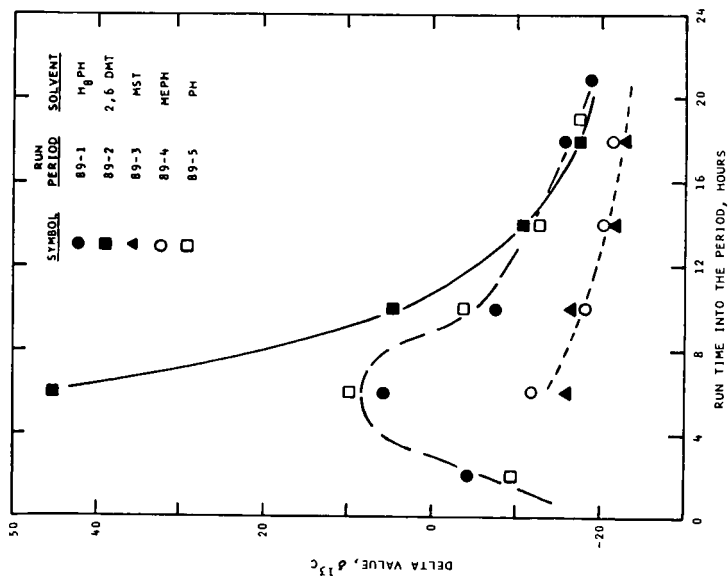


FIGURE 3: $\delta^{13}C$ LEVELS IN THE CONDENSATE SAMPLES OF RUNS 89-1 THROUGH 89-5

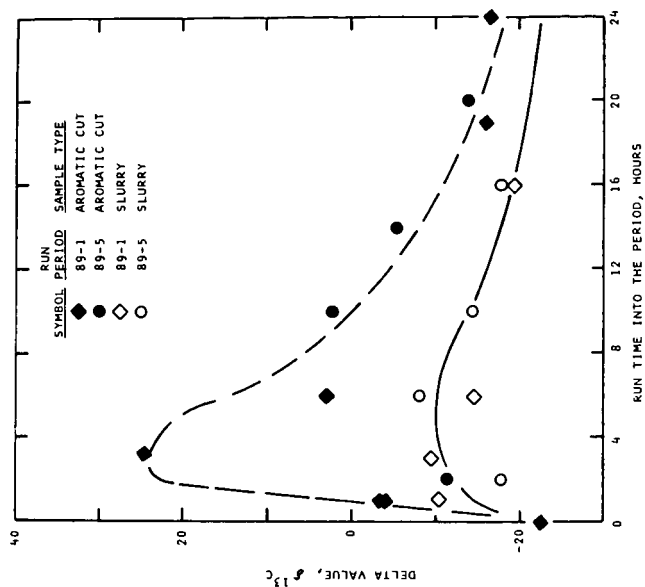


FIGURE 4: $\delta^{13}C$ LEVELS IN SAMPLES OF PRODUCT SLURRY AND THE AROMATIC CUTS DERIVED FROM THE SLURRY